

*A Theory of the Chemical Action of the Electric Discharge in
Electrolytic Gas.*

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Introduction.

In some previous papers* experiments have been described establishing various results when an electric discharge passes through a mixture of hydrogen and oxygen at low pressures. The results, which were very complicated, suggested a theory which satisfactorily explained them and throws a light upon the manner in which chemical effects are brought about by an electric discharge.

The experiments to be recorded in the present paper were undertaken with the object of testing the theory further and of providing data for developing it. But before describing the new experiments it will probably be useful to sketch the results of the previous experiments.

In the first place, explosive gases do not explode even partially when their pressure is below a certain value which naturally varies† with the gas. That value in the case of electrolytic gas lies between 40 millimetres and 80 mm. When the pressure is less than 40 mm. and an electric discharge is passed through the hydrogen and oxygen the gases begin to combine with great regularity. The amount of the chemical action, *i.e.* the mass of the water vapour formed, is proportional to the quantity of electricity passed through the gaseous mixture, so long as the circumstances of the discharge, including pressure, current, and the distance between electrodes, are constant. This result, which bears only a faint resemblance to Faraday's law of electrolysis, has nothing apparently in common with the law of mass action, for the rate of formation of the chemical product of a given current, instead of always increasing with the concentration, can under certain conditions be absolutely diminished by greatly increasing the pressure. In addition, the chemical action is independent of the nature of the electrodes and is not confined to their neighbourhood but takes place at all points of the discharge.

* P. J. Kirkby, 'Phil. Mag.,' February, 1904, January, 1905, March, 1907.

† Thus Mr. J. E. Marsh and the writer have recently found that azoimide explodes at above 10 mm., but not much below that pressure.

Chemical Activity Defined.

In the case of a steady long cylindrical discharge between two parallel plate electrodes, very different chemical effects are produced by the different parts of the discharge. It seems necessary here to introduce a new expression in order to describe them. Let P be any point in the discharge, and let two planes be imagined parallel to the electrodes, one containing P , the other a very short distance h from the first plane. Then the mass of the chemical product,* one only being assumed, formed after unit quantity of electricity has crossed (between the electrodes and therefore) between the planes divided by h will be called in this paper the *chemical activity at the point P* . More briefly, the chemical activity at a point may be defined as the mass of the chemical product resulting from the flow per cm. of unit quantity of electricity past the point; and this varies from point to point. The line-integral of this quantity between the electrodes, *i.e.* the mass of the chemical products resulting from the passage of unit of electricity between the electrodes, will be called the *total chemical activity* of the discharge.

The chemical activity is far greater near the cathode† than at any other point of the discharge. Across the cathode fall the total activity is nearly constant,‡ being independent of the pressure and electrodes (size and material). The chemical activity diminishes as the point recedes from the cathode; and at a distance of about 1 or 2 cm., when the gas is at a few millimetres pressure, it is scarcely appreciable§ until the positive column|| is reached.

At points within the positive column the chemical activity is constant or very nearly constant.¶ Now the positive column can be lengthened** without appreciably changing any other circumstance of the discharge,

* In the case of electrolytic gas nearly, but not quite, the whole of the chemical product of the discharge is water. For after two-thirds or three-quarters (according to the nature of the electrodes) of a given mass of the gas was formed into water under an electric discharge, the water being absorbed by P_2O_5 , the union of the remainder under the discharge showed signs of departing from the laws which related to pure electrolytic gas ('Phil. Mag.,' January, 1905, p. 183). This leads to the conclusion that at least 95 per cent. of the chemical product is water.

† P. J. Kirkby, 'Phil. Mag.,' March, 1907.

‡ 'Phil. Mag.,' January, 1905.

§ These results are deduced from the curves given, 'Phil. Mag.,' March, 1907.

|| The "positive column" is that region of a fairly long discharge where the electric force or potential-gradient is constant or nearly constant. It is easily recognised by the eye as a long more or less luminous cylinder, sometimes striated, of a colour peculiar to the gas. It extends from a distance (varying with pressure) of several centimetres from the cathode up to the anode. Thus at a pressure of 1 mm. it begins at about 7 cm. from the cathode.

¶ 'Phil. Mag.,' March, 1907.

** *Ibid.*, and 'Phil. Mag.,' April, 1908.

namely, if the electric force in the column is Y volts per centimetre and it is desired to increase the length of the positive column by d cm., it is merely necessary to increase the distance between the electrodes by d cm. and to add Yd volts to the battery, and with no other change the discharge will be the same as before, except that the positive column will be d cm. longer. Hence it is possible to deduce the chemical activity of the positive column by estimating the amounts of the chemical products produced by passing unit quantity of electricity through the gas by two separate discharges, passed at the same pressure, and differing only in the length of their positive columns, and then by dividing the difference in amount of these two chemical products by the difference of the lengths of the two positive columns. The result will be the chemical effect per centimetre of the positive column per unit quantity of electricity passed through it, or the chemical activity at any point of the positive column.

The chemical activity of* the positive column presents some striking features. It does not always increase with the pressure. Thus from previous experimental results† it proved to be twice as much for the pressure 1.4 mm. as for the pressure 4.5 mm. In fact the paradoxical result that the same current, passed for the same time, in hydrogen and oxygen can under certain conditions produce a greater mass of water when the pressure has certain values than when the pressure is much greater than those values is, perhaps, entirely due to the reactions within the positive column.

All these effects which are purely experimental have been accounted for by the theory suggested by the writer in previous papers,‡ namely, that the ions which constitute the electric current dissociate into uncharged atoms those molecules of the gas which they strike with adequate velocity and under favourable conditions, and that the atoms rearrange themselves according to dynamical and chemical necessities.

This theory can be tested and developed when the chemical activity is known of a uniform current flowing in various uniform fields of force through combining gases at different pressures, and such a field exists in the non-striated positive column of a long cylindrical discharge. It would of course be preferable to dispense with a gaseous discharge if it were possible to measure the chemical effects of such currents as can be made to pass in a uniform field of force without disturbing the uniformity of the field, such

* *Of* is used as an abbreviation for *at any point of* in the case of the positive column, with the understanding that the chemical activity is constant throughout it, analogously with the expression "potential of a conductor."

† 'Phil. Mag.,' March, 1907.

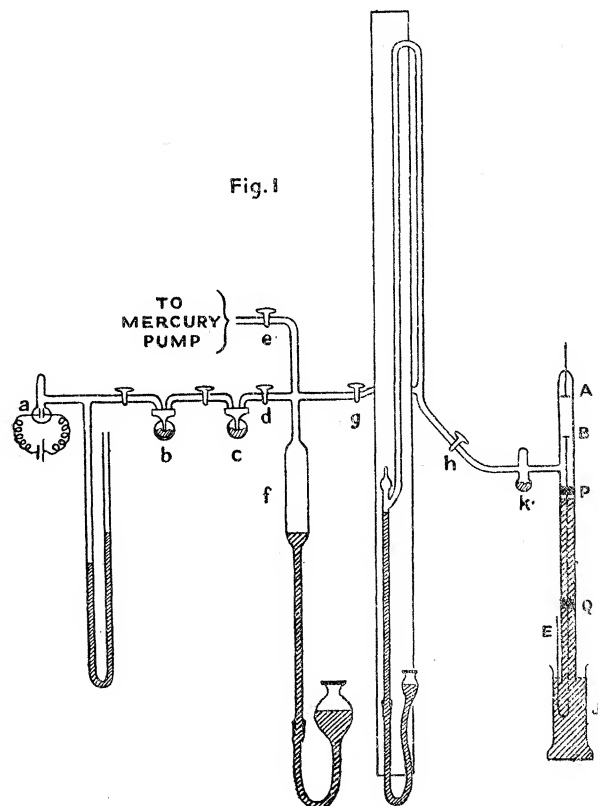
‡ 'Phil. Mag.,' February, 1904, etc.

as those produced by means of the Röntgen rays or ultra-violet light. But the chemical effects of the latter kind of currents would be far too small to be detected. Hence, in order to obtain experimental data, it has proved necessary to determine the chemical activity of the positive columns of various discharges.

Thus the experiments recorded in this paper chiefly deal with positive columns and were undertaken to determine simultaneously both the chemical activity and the electric force within positive columns corresponding to different currents and pressures.

The Apparatus.

The scheme of the apparatus is shown diagrammatically in fig. 1. The mixed gas ($2\text{H}_2 + \text{O}_2$) was generated in the closed vessel *a* by the electrolysis



of pure barium* hydrate, was then dried over phosphorus pentoxide in the drying vessel *b* and again in *c*, and was then passed into the discharge-tube

* Gas thus prepared is remarkably pure. H. B. Baker, 'Trans. Chem. Soc.,' 1902, vol. 81.

ABP. The latter, which was designed to permit the motion of the anode B (the cathode A was fixed), was a long vertical glass tube, about 2.4 cm., inner diameter, supported in a jar J full of mercury. Fig. 1 shows the tube partly filled with mercury, as it was during the experiments, which were all made at low pressures (less than 2 mm.). The distance of the top of the mercury from the cathode A, a distance which varied of course with the barometer, was then about 40 cm. The anode B was supported by a stout steel rod which passed through the fixed steel guides P, Q, and, bending round in the mercury of the jar J, terminated at E. Thus B could be raised or lowered by raising or lowering E.

Both electrodes were made of pure silver faced with a layer, 0.25 mm. thick, of pure gold and were intended to prevent oxidation with its disturbing effects. They were made by Messrs. Johnson and Matthey, of Hatton Garden. The anode, which had to move freely along the tube, was 2 cm. in diameter, while the fixed cathode was rather larger, fitting fairly close to the tube.

The side-tube by which the gas entered the discharge-tube was fused to that tube below the lowest position of the anode, so that the uniformity of the discharge might not be disturbed; and, being short and comparatively wide, it permitted the water vapour formed by the discharge to diffuse rapidly to the phosphorus pentoxide contained in the little glass vessel *k* to which its other end was fused. The object of the tap *h* on the other side of *k* was to prevent the water vapour escaping before coming in contact with the phosphorus pentoxide. When *h* was opened the McLeod gauge shown in fig. 1 and an ordinary manometer, not shown, became connected with the discharge-tube ABP.

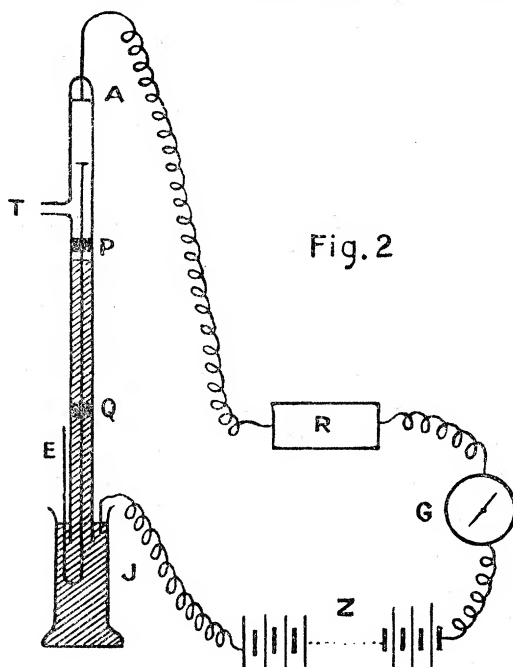
The tap *g* was inserted to cut off the discharge-tube with the McLeod gauge and manometer from the test of the apparatus; for the quantity of the chemical product resulting from the discharge was measured by finding the fall of pressure produced by the discharge, and it was important to increase this effect by reducing the space where the pressures were measured.

The large tube *f*, which could be filled with mercury, was added to the apparatus for the purpose of making accurate adjustments of the pressure in the discharge-tube.

Since the method, as will appear below, essentially involves the determination of *differences* of small pressures, it was of primary importance to measure the pressures with the utmost accuracy. For this purpose the McLeod gauge was fitted with an arrangement for raising or lowering the reservoir of mercury with a slow screw motion after rough adjustment, and a mirror was placed beside the zeros of the gauge, so that with the help of a lens the level of the mercury could be raised accurately to the zero without

errors of parallax. In this way small pressures could be read to about 0.001 mm.

The electrical connections are shown diagrammatically in fig. 2. Z was a battery of 1700 volts or less, and R was sometimes as much as 3 megohms.



G was a D'Arsonval galvanometer such that the current corresponding to a deflection of the spot of light through about 67 mm. was 10^{-4} ampère, which was the order of the currents used (see Table I).

Method of Experiment.

The hydrogen and oxygen having been introduced and the anode fixed at a certain distance, usually about 30 cm., from the cathode, the pressure was adjusted and carefully determined. A steady current C of the order 10^{-4} ampère, but otherwise arbitrary, was then passed between the electrodes for a few seconds t (between 5 and 12). Such small currents as this were necessary, for in order to extend previous results it was necessary to work with lower pressures than had hitherto been used, pressures even so low as 0.2 mm.; and larger currents, on account of their greater chemical effects, would not have remained approximately constant for a time long enough to measure accurately with a stop-watch. Another great advantage in working with very small currents is that the positive column is free* from striae

* This does not appear to have been noticed before.

when the current is below a certain value, at least in the case of low enough pressures, and in the absence of striæ the field of force within the positive column is quite uniform.

The effect of the passing of the current is that water vapour is formed which diffused to, and was absorbed by, the phosphorus pentoxide in the vessel to the left of the tube T in fig. 2. This diffusion takes place very rapidly at low pressures, so that the water vapour was quickly removed. After a short interval, then, to permit of this diffusion, the pressure was again very carefully determined. The mean of the initial and final pressures was taken as the pressure p of the observed effect and the difference, Δp , between the initial pressure and the final pressure measures the chemical action produced by the passage of the Ct units of electricity through the gas. Thus $\Delta p/Ct$ or $\Delta p/\Delta Q$, the fall of pressure per coulomb, is obtained.

During the discharge the distance from the cathode of the point where the positive column began was noticed; and for the second experiment the anode was moved about d cm. nearer, d being rather less than the length of the positive column in the first discharge (and usually about 20 cm.), so that for the second experiment the positive column was very short. The pressure was then readjusted so that approximately the same mean pressure p might result for the second discharge as for the first, and the battery was also diminished from (say) Z_1 to Z_2 , so that the same current might pass as before. Thus everything was the same for the two experiments except the voltage of the battery and the distance between the electrodes. After the passage of the current for the second time, $\Delta p/\Delta Q$ was again determined as before.

The difference between the two values of $\Delta p/\Delta Q$ divided by d is obviously the fall of pressure per coulomb passed through 1 cm. of the positive column in question at the pressure p , and hence is proportional to the chemical activity of the positive column; and the electric force Y in the particular positive column is simply the difference of voltage of the battery in the two cases, namely, $Z_1 - Z_2$, divided by d .

The first of these two observations, as already stated, was made with arbitrary current C ; but in the second experiment with diminished distance between electrodes the same current had to be accurately reproduced in order to determine the correct value of Z_2 . In practice this result is easily achieved by means of two observations with slightly different batteries giving two currents, one less, the other greater, than C , and by interpolation. Such precautions would be unnecessary if the electric force were known and only the values of $\Delta p/\Delta Q$ were required, for the latter changes but little with

the current when the positive column is very short, as Table I below shows.

In many cases a third value of $\Delta p/\Delta Q$ was obtained with the distance between the electrodes the mean of the previous distances and the same pressure and current as before. Its value ought to be the mean of the previous values, since the positive column contributes to the total chemical effect an amount proportionate to its length. It was determined as a verification of the other two values and will help to indicate their accuracy, but was not used in deducing the chemical activity of the positive column.

Results of the Experiments.

The values of $\Delta p/\Delta Q$, determined in the manner just described, with two or more different distances D between the electrodes, but the same current C, are given in Table I for various pressures.

The significance of $\Delta p/\Delta Q$ depends of course upon the cubical capacity of the part of the apparatus where the falls of pressure produced by the current took place, viz., the part to the right of the tap *g*, fig. 1. This capacity was 474 c.c., or rather it varied within about 1.3 per cent. of this value, changing slightly with the barometer and with the length of the rod supporting the anode above the mercury. It is, however, convenient to express the results absolutely, *i.e.* independently of the apparatus. This might be done by multiplying $\Delta p/\Delta Q$ by 1000/474 so as to give the fall of pressure per coulomb that would take place in an apparatus of capacity 1 litre. But the simplest course, in view of the subsequent discussion, is to find how many molecules of water vapour* are formed by the passage through the gas of the atomic quantity of electricity, namely, the charge carried by a negative ion. This number is denoted by W. Now it is easy to show that approximately

$$W = 1.69 \frac{\Delta p}{\Delta Q}.$$

For if N is the number of molecules in 1 c.c. of gas at 760 mm. pressure and 15° temperature, and *e* the charge on an ion in electrostatic units, $Ne = 1.22 \times 10^{10}$.† And in this apparatus of 474 c.c. a fall Δp of the pressure of electrolytic gas is due to the disappearance of $N \times 474 \times \Delta p/760$ molecules of $2H_2 + O_2$ and so to the formation of two-thirds that number of molecules of water vapour; while ΔQ coulomb is $\Delta Q \times 3 \times 10^9/e$ times the atomic (or electronic) charge. Hence the number of molecules of water formed by the

* It is assumed that any other product of the discharge than water vapour is negligible. See the third footnote to this paper.

† Townsend, 'Phil. Trans.' A, 1899.

passage of the atomic charge between the electrodes (W) is immediately found to be $1.69\Delta p/\Delta Q$.

The values of W are given in Table I. Now if the least value of W corresponding to a certain pressure and current in Table I is subtracted from the greatest, and the result divided by the difference of the two values of D , it is clear that the quotient is the number of molecules of water resulting from the passage of the atomic charge through 1 cm. of the positive column. This number is denoted by w . Now the chemical activity of the positive column is the mass of the chemical product per unit length of the column and per unit quantity of electricity that passes. Hence w is proportional to the chemical activity of the positive column, and is in fact *equal* to it if the molecule of water vapour is taken as the unit mass and the atomic charge as the unit of electrical quantity. Similarly W will measure, or equal, the total activity of the discharge.

The values of w thus calculated, corresponding to the positive columns of various discharges which are fully defined by the pressure and current stated, are given in Table I in the sixth column.

The corresponding values of the electric force (Y) within the positive column are given in Table I. They were all determined by direct experiment simultaneously with w , except in one case, where Y was found for a slightly different value of p , and a correction had to be made. Although in general Y is a function of the current as well as of p , yet the currents of Table I are so small that Y is practically a function of p only. This is proved by fig. 3, in which the points determined by plotting Y against p determine a curve accurately. This curve has proved a useful check upon the values of Y , and has supplied one missing value as already alluded to. Still it is important to determine Y by direct experiment, instead of relying upon the graph, in case anything may occur to disturb the normal value of Y , as in one case corresponding to $p = 1.4$, where the point determined by p , Y , does not fall upon the curve of fig. 3.

The values of w/p , Y/p , are given in Table I for reasons to follow. The last column of the table shows where the positive columns were observed by the eye to begin; these observations decided the least value of D , which had to exceed the distance of the beginning of the positive column from the cathode.

The rather complicated notation-symbols which it has been necessary to employ are here collected and once more fully explained for the purpose of reference.

The reason why so many observations were made with pressures near to 1.4 mm. will be given later. One result must be noticed here, namely,

Table I.

p .	$C \times 10^3$.	D.	$\Delta p/\Delta Q$.	W.	w .	Y.	w/p .	Y/p .	q .
1.98	0.474	{ 24 16 8	{ 17.2 10.7 5.5	{ 29.1 18.1 9.3	{ 1.24	32.5	0.63	16.4	6.5
1.75	0.44	{ 31.5 6.5	{ 21.0 4.4	{ 35.5 7.4	{ 1.12	31	0.64	17.7	
1.67	0.428	{ 30 19 8	{ 20.5 13.1 5.2	{ 34.6 22.1 8.8	{ 1.17	30.9	0.70	18.5	6.5
1.4	0.315	{ 24 8 25	{ 13.85 5.07 19.5	{ 23.4 8.57 32.9	{ 0.93	25	0.66	17.9	
1.4	0.257	{ 16 7 25	{ 11.7 5.3 17.4	{ 19.8 8.95 29.4	{ 1.33	27.3	0.95	19.5	6.5
1.32	0.358	{ 7 25 17.1	{ 4.8 17.1 28.9	{ 8.1 28.9 19.8	{ 1.18	27.4	0.90	20.8	
1.28	0.274	{ 16 7 28	{ 11.7 4.9 21.5	{ 19.8 8.3 36.3	{ 1.14	26	0.895	20.3	6.5
1.21	0.227	{ 8 31.5 19.5	{ 5.9 21.3 13.3	{ 10 36 22.5	{ 1.32	25.5	1.09	21.1	
1.06	0.285	{ 7.5 31.5 8.5	{ 5.2 20.2 5.6	{ 8.8 34.1 9.5	{ 1.13	23	1.07	21.7	7.0
0.88	0.172	{ 31.5 8.5 31.5	{ 20.2 5.6 19.3	{ 34.1 9.5 32.6	{ 1.07	21	1.22	23.9	
0.6	0.133	{ 8.5 31.5 10.5	{ 5.3 19.3 18.1	{ 9.0 32.6 30.6	{ 1.03	17	1.72	28.4	8
0.48	0.098	{ 31.5 10.5 31.5	{ 18.1 5.9 16.5	{ 30.6 10.0 27.9	{ 0.98	15.3	2.04	31.9	8.3
0.35	0.123	{ 21 10.5 31.5	{ 10.3 5.4 15.6	{ 17.4 9.1 26.4	{ 0.90	12.3	2.56	35.2	
0.291	0.119	{ 11.5 21.5 11.5	{ 5.9 10.6 5.9	{ 10.0 17.9 10.0	{ 0.82	11.3	2.82	38.9	10.5
0.242	0.094	{ 31.5 11.0 31.5	{ 13.8 5.5 13.1	{ 23.3 9.3 22.1	{ 0.68	10.5	2.82	43.4	10.5
0.193	0.106	{ 11.5 31.5 11.5	{ 5.4 13.1 5.4	{ 9.1 22.1 9.1	{ 0.65	9.6	3.37	49.7	

NOTATION OF TABLE I.

p = the mean pressure during the discharge in millimetres of mercury.

Δp = the fall of pressure produced by the discharge.

C = the current of the steady discharge in ampères, so that the second column gives the current in milliampères.

ΔQ = the quantity of electricity in coulombs passed through during the discharge (Ct).

D = distance between the electrodes.

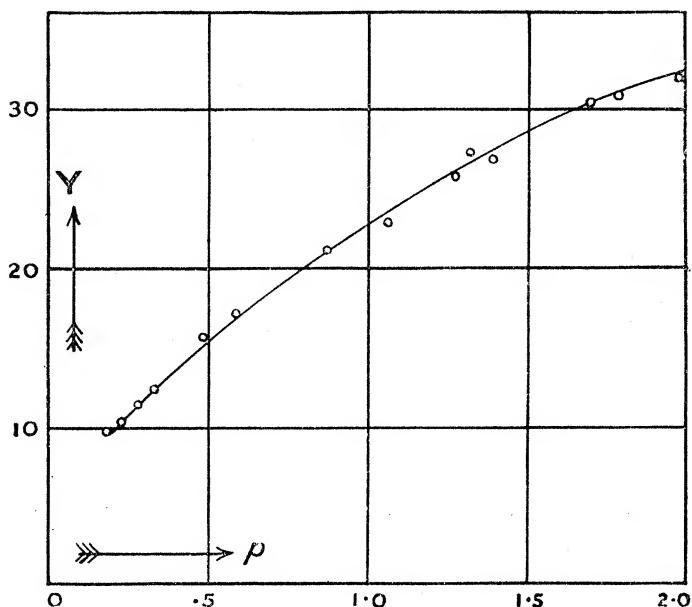
W = the number of molecules of water produced by the passage of the atomic quantity of electricity between the electrodes = $1.69 \times \Delta p/\Delta Q$ = the total chemical activity of the discharge.

w = the difference of the greatest and least values of W divided by the difference of the corresponding values of D = the chemical activity of the positive column.

Y = the electric force (volts per centimetre) of the positive column.

q = the distance from the cathode of the nearest part of the positive column.

Fig. 3



the two discrepant values of w corresponding to the same pressure 1.4 mm. This discrepancy lies far beyond the errors of observation, but is fully explained by the concomitant discrepancy in the values of Y , which is possibly the effect of the presence of water vapour. In fact each value of w is related to the corresponding value of Y in the manner required by the theory within the limits of experimental error.

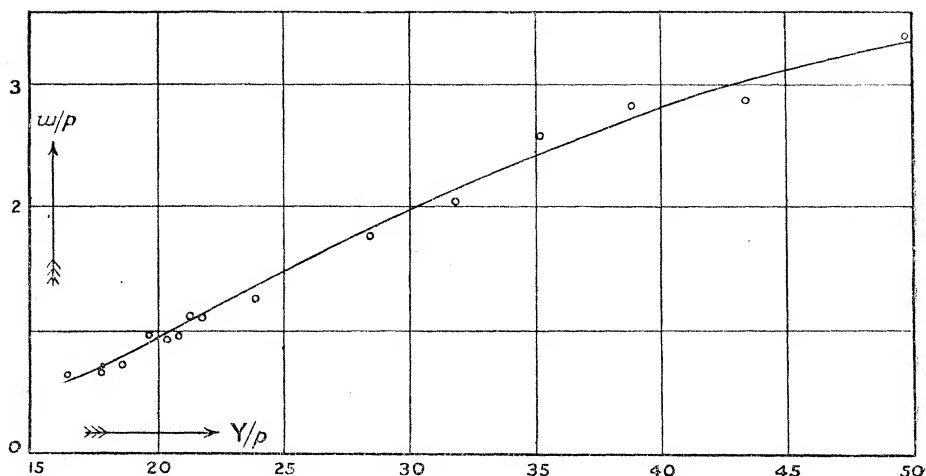
Limits of Experimental Errors.

The errors involved in the various values of $\Delta p/\Delta Q$ and therefore of W were in most cases probably less than 5 per cent. The largest values corresponding to the largest values of D when repeated seldom differed by more than that, and sometimes the agreement was much closer. If the same order of error is assumed in the least values of W , which are a small fraction (generally about one-third or one-fourth) of the greatest values, the values of w , which depend on the difference of greatest and least values, would have a rather greater error-limit, 7 or 8 per cent., or even more in a few cases.

Deductions from Table I that are Independent of Theory.

If the values of w/p given in the table are plotted against the corresponding values of Y/p , the points so obtained determine a simple continuous curve. This is shown in fig. 4.

Fig. 4



It follows that w/p is a function of Y/p , and that the relation between these two variables is *independent of the current*, for the current was arbitrary and varied by several hundred per cent., while the points plotted in fig. 4 fall upon the curve within the limits of experimental error.

This result proves definitely that the observed chemical effects in the positive column are not directly due to recombination* of ions, for the number of recombinations per cubic centimetre would increase with the square of the current, since the force and therefore the velocity of the ions are very little affected by the current.

It also proves that these chemical effects are not due to any internal radiation, such as perhaps the "entladungstrahlen," set up in the positive column by the recombination of ions, for the intensity of such a radiation would probably be proportional to the square† of the current, and certainly could not have a chemical effect dependent only upon the quantity of electricity passed through the gas.

Another result, which is quite independent of any theory of the chemical action, is immediately deducible from Table I. It is this, that the atoms of a molecule of oxygen when dissociated from one another are not charged electrically.

This follows at once from the fact that the chemical output of the

* *E.g.*, to the union of a hydrogen positive ion with a hypothetical negative ion consisting partly of an oxygen atom. It is, however, very probable that a negative ion can only exist in the corpuscular state in a region where Y/p is so large as in Table I.

† See H. A. Wilson, 'Phil. Mag.,' July, 1903, who gives reasons for concluding that the "entladungstrahlen" are due to the recombination of ions.

positive column is proportional to its length. Now, when the pressure is 0.5 mm., the table shows that $w = 1$. Therefore one molecule of water results from the passage of the atomic charge through 1 cm. of the positive column. Hence, at least one molecule of oxygen is dissociated by the passage of the atomic charge through 2 cm. of the positive column. Now, if the dissociated atoms were charged, one positively, the other negatively, the former would be carried along with the current as a positive ion, while the electron attached to the latter would be torn away from it and add itself to the current. The result would be that an increase of only 2 cm. of the positive column would double the current, and an increase of 18 cm. would multiply the current by ten. In fact, the disturbance produced in the discharge by the chemical action would, if the atoms when dissociated were charged, always be enormous,* whereas it is certain that the chemical effects of the discharge only affect the discharge very slightly, and in a secondary manner by changing the pressure and the composition of the gas.

These considerations prove definitely that the atoms of oxygen, however they come to be dissociated previous to their combining with hydrogen, are during their dissociated state uncharged. Hence their union with hydrogen cannot be attributed to electrostatic forces.

It naturally follows that the forces which bind the atoms of oxygen into molecules of various substances are not electrostatic attractions, and that, if they are of electrical origin, they are electromagnetic, the atoms not being subject to electric force.

Theoretical Consideration of Table I.

It will now be shown that the results recorded in Table I confirm the theory suggested in the writer's previous papers and already stated in this, namely, that the chemical effects of an electric discharge are the result of the collisions of the ions constituting the current with the molecules of the gas, that the molecules, when struck by an ion with sufficient velocity, and under favourable conditions, are broken up into *uncharged* atoms, which are then free to recombine in accordance with dynamical and chemical necessities.

In the preceding paper on this subject it was guardedly assumed that the chemical effects in the positive column are entirely due to the motion of corpuscular negative ions (or electrons). Probably positive ions, by their collision with the gas molecules, are also responsible for similar chemical

* This remark would still be true even if the hypothetical negatively charged atom could move as such in regions where the ratio of electric force to pressure is so great as in these positive columns. It is, however, assumed above, in accordance with well-established results, that negative ions are in the corpuscular state in such regions.

effects when they move through a region where the ratio of the electric force to the pressure exceeds a certain value, as will be shown later on. But the theory that the chemical effects observed in the positive column are entirely due to the motion of the electrons leads to simple and coherent results which strongly support it.

According to this theory, then, w , which was defined to be the number of molecules of water vapour formed by the transit of the atomic charge through 1 cm. of the positive column, becomes the number of molecules of water vapour formed by the motion of a negative ion through $u_1/(u_1+u_2)$ cm., where u_1, u_2 , are the velocities of the negative and positive ions in the positive column. Now u_2/u_1 is quite negligible in regions where the ratio of electric force to pressure is so great as in the positive columns of Table I.* Therefore the theory makes w the number of water-vapour molecules formed by an electron's motions through 1 cm.; and it remains to show that the observed values of w are connected with those of p and Y as the theory requires.

In what follows† it is assumed that, owing to their very small mass, the electrons are brought practically to rest by their collisions with the gas molecules. It is also assumed (an assumption usually made and easy to justify) that the fields of force here considered impress such a high velocity upon the electrons that the gas molecules may be considered relatively at rest. Now the collision of an electron with a molecule of oxygen cannot have the effect of separating the atoms unless the energy of the electron at collision exceeds the energy of formation of the oxygen molecule, which will be denoted in this paper by η ergs. But besides this condition it is natural to suppose that the electron will not dissociate the molecule unless it collides with a certain minimum velocity.‡ Let V volts represent the potential difference through which the ion must fall to acquire this velocity, then

$$eV/300 > \eta, \quad (1)$$

e being the charge in electrostatic units of the electron. Hence in a field of force, Y volts per centimetre, the electron must traverse a free path of V/Y cm. or more before colliding with an oxygen molecule if it is to acquire the

* R. T. Lattey, 'Roy. Soc. Proc.,' A, 1910, vol. 84. His numbers make $u_2/u_1 = 0.04 qp$ when this ratio is 0.1. Hence, when Y/p is so large as in Table I, u_2/u_1 is extremely small.

† Cf. J. S. Townsend, 'Phil. Mag.,' February, 1901, whose method is here adapted.

‡ The genesis of *uncharged* atoms from the molecules of oxygen by the impact of electrons must not be confused with the genesis of ions by collisions. The former are produced in large numbers when the value of Y/p is so small that only very few ions can be produced. Thus, when $Y/p = 20$, each ion produces on an average 0.94 water molecule per centimetre when p is 1 mm.; for the same force and pressure the number of ions generated in air would be probably 0.01 per cm., and in hydrogen about 0.05.

necessary velocity of impact to break up the molecule into atoms. Again, let the electron make x collisions with oxygen molecules in moving through 1 cm. in electrolytic gas ($2\text{H}_2 + \text{O}_2$) at a pressure of 1 mm. Then it will make px such collisions in the same gas at p mm. pressure. Now it is well known that of N_1 free paths $N_1 e^{-n}$ exceed n times the mean free path l , i.e., $N_1 e^{-nl}$ exceed the distance c . If then $N_1 = px$, $c = V/Y$, $l = \lambda/p$, where λ is the mean free path of the electron in electrolytic gas at 1 mm. pressure, it is clear that the electron will, in moving through 1 cm. of the gas, strike $pxe^{-Vp/Y\lambda}$ molecules of oxygen with velocity great enough to atomise them. But the hit to be effective may have to fulfil other conditions. In that case the number of molecules dissociated will bear a constant ratio to the number struck with adequate velocity. Hence the number of atoms of oxygen dissociated by the motion of the electron through 1 cm. will be $2kpxe^{-Vp/Y\lambda}$, where k , the constant ratio mentioned, is an absolute constant less than or equal to unity.

If each of these atoms of oxygen were to unite with hydrogen to form a molecule of water it would follow at once that

$$w = 2kpxe^{-Vp/Y\lambda}, \quad (2)$$

for, as already explained, w , as originally defined, becomes, from the point of view of the theory, the number of molecules of water vapour formed by the motion of the electron through 1 cm., and if a constant percentage of the liberated oxygen atoms go to form water-vapour molecules, then

$$w = 2\mu pxe^{-Vp/Y\lambda}, \quad (3)$$

where $\mu < k < 1$.

The theory, however, leads presently to the conclusion that an atom of oxygen can combine directly with a hydrogen molecule without the latter's previous dissociation; in other words, if any relative displacement of the atoms in a hydrogen molecule is necessary before the synthesis of water can take place, such a displacement can be effected by the collision of the oxygen atom with the molecule of hydrogen. That being so, a detached atom of oxygen will most probably give rise to a molecule of water vapour, for its chance of meeting a hydrogen molecule is obviously much greater than its chance of meeting another atom of oxygen, and the probability of its uniting with oxygen is proved to be small by the small amount of ozone that is generated by the discharge. The conclusion to be drawn is that μ is nearly the same as k .

If w/p , Y/p are denoted by w_1 , Y_1 , equation (3) becomes

$$w_1 = ce^{-V/Y_1}, \quad (4)$$

where

$$c = 2\mu x, \quad (\mu < 1), \quad (5)$$

so that c is less than twice the number of collisions which an electron makes with oxygen molecules in moving through 1 cm. in electrolytic gas at 1 mm. pressure.

Now it is easy to deduce approximate values for λ and x from the experimental results of Prof. J. S. Townsend and Mr. H. E. Hurst, according to which an electron moving rapidly under electric force makes* 15.2 collisions per centimetre in air at 1 mm. pressure and 13.6 collisions in nitrogen at the same pressure. Hence in nitrogen at 0.79 mm. pressure an electron would make 13.6×0.79 collisions per centimetre = 10.75, and therefore $15.2 - 10.75$ or 4.45 collisions per centimetre with the molecules of oxygen if moving in oxygen at 0.21 mm., and therefore would make 7.06 collisions in oxygen at 0.333 mm. Hence an electron would make 7.06 collisions with oxygen molecules in passing through 1 cm. of electrolytic gas at 1 mm. pressure. Hence

$$x = 7.06. \quad (6)$$

It is, however, important to point out that the value of x thus deduced may have a very large percentage error. For instance, if the numbers 15.2, 10.75, involve moderate experimental errors of 3 or 4 per cent., their difference 4.45 *may* involve an error of more than 20 per cent. This would be unlucky, but an error of 10 per cent. is quite probable.

Again the electron makes† 5.5 collisions per centimetre in hydrogen at 1 mm. pressure, so that in electrolytic gas it makes $5.5 \times \frac{2}{3} = 3.67$ collisions with hydrogen molecules in moving rapidly through 1 cm.

Therefore

$$\lambda^{-1} = 7.06 + 3.67 = 10.7. \quad (7)$$

This value of λ^{-1} is infected with the large errors which may lie in the value 7.06 obtained for x . But fortunately a more exact knowledge of x and λ is not necessary in order to establish the complete agreement between the experimental results recorded in this paper and the theory suggested to explain them.

Agreement of the Theory with the Experimental Results.

Equation (4), $w_1 = ce^{-V/\lambda Y_1}$, agrees with the form of the curve drawn in fig. 4 if

$$V/\lambda = 42.7, \quad (8)$$

and

$$c = 7.9, \quad (9)$$

thus satisfying the condition of equation (5) that $c < 2x$, i.e. < 14.1 . This agreement is shown in Table II.

* J. S. E. Townsend, 'Phil. Mag.' [5], 1903, pp. 389—398; H. E. Hurst, 'Phil. Mag.', April, 1906.

† J. S. Townsend, *ibid.*

Table II.

Y_1	17	20	21·3	25	30	40	50
$7·9 e^{-42·7/Y_1}$	0·64	0·94	1·07	1·43	1·91	2·71	3·38
Ordinate of curve	0·64	0·92	1·08	1·44	1·96	2·8	3·36

Thus the curve defined by the equation

$$w_1 = 7·9 e^{-42·7/Y_1}, \quad (10)$$

the form of which is given by the theory, is practically the same as that determined by the points plotted in fig. 4, *i.e.* by the experimental results of Table I.

In connection with this agreement of the theoretical curve with the experimental, it is important to point out that small errors in Y_1 when Y_1 is considerably less than 42·7 may throw the corresponding point seriously off the curve, even if the corresponding value of w_1 is correctly determined, for equation (10) gives $\delta w_1/w_1 = (42·7/Y_1) \delta Y_1/Y_1$. This fact will explain the relatively large divergence from the curve of some of the points of smaller abscissæ in fig. 4. It was on account of these divergencies that so many points in this region of the curve were determined in order to ascertain the true position of the curve.

It may also be noticed that the curve (10) has only one inflexion, where $Y_1 = 21·3$, and that the curvature is convex to the left and concave to the right of it. The curve in fig. 4 has been drawn to satisfy these conditions, and it is, within the limits of error, the mean locus of the points plotted; but the curvature is too slight, and the exact position of the point to the extreme left too uncertain, for the reasons just given, to attach much weight to these considerations.

The Relation Between w , p , and Y Probably Absolute.

It follows from the preceding discussion that the theory is in complete agreement with experiment as far as it has been found possible to verify it. The obstacles to a more complete verification are inherent in the method and consist of the limited range of variation of w and Y , and the fact that it is not possible to vary Y , at least to any great extent, independently of p . On the other hand, the approximate relation (10) between w/p and Y/p is well supported by the few similar results* that were deduced by the writer from

* 'Phil. Mag.,' March, 1907. The value of Y corresponding to $p = 2·1$ was determined in this paper by a graphic method from the curve, p. 301, corresponding to the pressure 2·1 mm., as 40; but a revaluation by the same method shows that 37 would be nearer the mark. If this correction is made, the four pairs of values of Y/p , w/p , corresponding to the pressures 4·5, 2·1, 1·05, 0·65, satisfy equation (10) well enough.

some similar experiments which were made with a different apparatus and much greater currents, the forces in the positive columns being appreciably different at the same pressure. Thus the observed values of w are found to respond to any change that has arisen in Y . These considerations lead to the conclusion that the approximate equation (10), viz., $w/p = 7.9e^{-42.7/(Y/p)}$ between w , p , Y is probably an absolute relation; namely, it is a relation independent of the apparatus and not confined to positive columns but existing between the chemical effects of an electron's motion, through electrolytic gas ($2H_2 + O_2$) and in any field of electrostatic force Y , and Y and p . It is true that special conditions prevail in the positive column where these effects have been observed, and that a certain amount of recombination may be going on, so as to terminate the course of a percentage of the electrons that traverse it. That percentage is, however, probably* negligible; and in any case, ions are produced at exactly the same rate as they disappear, since everything is quite steady, so that the mean chemical effects attending the passage of the atomic charge through 1 cm. of the positive column must be the same as though that charge was carried by the same electron. Thus there is no reason to suppose that the relation (10) between w , p , Y , in the positive column would not equally exist anywhere else where there may be an electrostatic force Y .

Deductions from the Theoretical Equation.

The equation $w_1 = 7.9e^{-42.7/Y_1}$ leads to several results which will now be deduced.

(1) *Approximation to the Energy of Formation of an Oxygen Molecule.*—Since $V/\lambda = 42.7$ and $1/\lambda = 10.7$ by equations (8) and (7), therefore $V = 4$ volts.† That is, an electron must fall freely through at least 4 volts to acquire sufficient velocity to dissociate by impact an oxygen molecule into atoms. Hence by the inequality (1) η , the energy of formation of an oxygen molecule, is less than $(4e/300 =) 6.1 \times 10^{-12}$ ergs, since the charge e of an electron seems‡ to be nearly 4.6×10^{-10} electrostatic units; and since the present theory assumes that the electron is practically stopped by its collisions, so that nearly all its energy is imparted to the molecule struck, the limit, 6.1×10^{-12} ergs, should be fairly near to the actual value of η . This estimate is independent of the quantity of water

* Because of (1) the low pressures, (2) the very high velocity of the stream of electrons for such large values of Y/p , as recently proved by Mr. R. T. Lattey (*loc. cit.*), (3) the very small current density of that stream, which is necessitated by (2).

† The limit 6.4 volts was previously deduced by the writer by rather different reasoning, 'Phil. Mag.' March, 1907.

‡ Rutherford, Address to British Association, 1909; R. T. Lattey, 'Phil. Mag.' July, 1909.

vapour present (which it might perhaps be thought would lower the energy of formation of a molecule), for the amount of water vapour present depends on the strength of the current, and equation (10), from which the estimate is deduced, is independent of the current. But it is, of course, subject to any correction necessitated by possible errors in the value of λ .

The limit just found for η receives support from other researches. Berthelot* found by experiments on the oxidation of arsenious acid that when two gramme-molecules (96 grammes) of ozone passed into oxygen 61400 calories of heat were liberated. From this datum a value for η , which is probably a lower limit, can be obtained. Let it be assumed provisionally that when two molecules of ozone pass into three of oxygen the energy set free is simply due to the formation of one molecule of oxygen. Then, when 1 c.c. of ozone is transformed into oxygen, $\frac{1}{2}N\eta$ ergs of energy will be liberated, where N is, as usual, the number of molecules of a gas in 1 c.c. at 760 mm. pressure and 15° centigrade. But Berthelot's numbers give 1.31 calories as the heat of transforming 1 c.c. of ozone at 760 mm. and 15° C. into oxygen.

Therefore $\frac{1}{2}N\eta = 1.31 \times 4.2 \times 10^7$ ergs and $Ne = 1.22 \times 10^{10}$.

Hence, since $e = 4.6 \times 10^{-10}$, $\eta = 4.1 \times 10^{-12}$ q.p.

This value has been obtained by neglecting the work required to detach one atom from the ozone molecule, and by assuming that the potential energy of the remaining pair of atoms is unaltered. If, however, a substantial amount of work is needed to detach the atom, the number obtained for η is too small, unless the rearrangement of the remaining atoms liberates enough energy to balance that lost in detaching the one atom from the molecule. Probably then η exceeds 4.1×10^{-12} ergs.

Mulder and Van der Meulen,† revising Berthelot's work, obtained rather larger values which would lead to 4.4×10^{-12} ergs: and Van der Meulen, by direct determination of the heat of decomposition of ozone, obtained still higher values for the same quantity, which would lead to 4.9×10^{-12} ergs, instead of the 4.1×10^{-12} ergs deduced above, as probably a lower limit for η . If the value 4.5×10^{-12} ergs is adopted as a mean and taken as a lower limit for η , it follows that the superior limit 6.1×10^{-12} ergs found above for η is fairly close to its true value as the theory suggests.

(2) *Hydrogen must Combine Directly with Atomic Oxygen.*—The equation $w_1 = 7.9 e^{-42.7/Y_1}$, involves the consequence that if Y_1 is great enough, w_1 approaches 7.9 as its limiting value. That is, an electron might, in

* 'Thermochimie,' 1897, vol. 2, p. 44. This was a revised estimate of the original value given, 'Ann. Chim. Phys.' [5], vol. 10, p. 164.

† 'Rec. Trav. Chim. Pays Bas,' vol. 1, pp. 65 and 73.

moving through 1 cm. of electrolytic gas at 1 mm. pressure under a large force, cause the formation of 7.9 molecules of water. But an electron has been shown (see equation (7)) to make only 3.7 collisions with the hydrogen molecules in so moving, and therefore could not produce more than 7.4 atoms of hydrogen, which, if it were necessary for the synthesis of water to bring the hydrogen to the nascent or atomic state, would not be sufficient to produce more than 3.7 molecules of water vapour.

On the other hand (see equation (6)) an electron in moving through 1 cm. of electrolytic gas at 1 mm. pressure makes 7.06 collisions with oxygen molecules, so that if only 4 out of these collisions dissociated the molecules into atoms, there would still be enough detached oxygen atoms for the production of the 7.9 molecules of water.

It follows from these considerations that an atom of oxygen is capable of uniting directly with a *molecule* of hydrogen. In other words, if the atoms in a hydrogen molecule need to be relatively displaced previous to the formation of water, such a displacement can be effected by the collision of the free atom of oxygen.

This conclusion is supported by the form of equation (10), which requires that only one of the gases need be brought to the active state. For if the hydrogen had also to be atomised by ionic impact, the amount of water vapour would be proportional to the product of $2pxe^{-Vp/Y\lambda}$ and a similar term applicable to hydrogen (see equation (2)). Hence would

$$w/p^2 = ae^{-bp/Y},$$

(a, b , constants), and w/p^2 would be a function of Y/p : the latter result is inconsistent with one or two observations in this and the last paper, and the former does not appear to be reconcilable with the rest.

(3) *Energy of Formation of a Molecule of Water Vapour.*—From the two previous conclusions (1) and (2) it is possible to form an estimate of the energy of formation of a molecule of water vapour. For, as is well known, 1 gm. of hydrogen, uniting with oxygen to produce water vapour at laboratory temperature, liberates 29,000 calories of heat, that is 1.22×10^{12} ergs, and consists of $1.44 \times 10^{14}/e$ molecules, e being as before the atomic charge, e.s.u. Therefore the formation of each molecule of water vapour sets free 3.9×10^{-12} ergs. But when two molecules of water vapour are formed, one molecule of oxygen must be separated into atoms, costing between 4×10^{-12} and 6×10^{-12} ergs by (1). Hence the energy of formation of a molecule of water must lie between 5.9×10^{-12} and 6.9×10^{-12} ergs, being nearly 6.4×10^{-12} ergs. This estimate would have to be increased if it were necessary to suppose that a comparable amount of energy had to be

spent in dissociating into atoms a molecule of hydrogen. But by (2) this is not *necessarily* the case. According to this result the oxygen molecule is nearly as stable as one of water vapour, a result which accounts for the great stability of electrolytic gas at ordinary temperatures.

(4) *The Proportion of Effective Collisions.*—It was pointed out in the discussion of (2) that an electron would cause the formation of 7.9 molecules of water in moving through 1 cm. of electrolytic gas at 1 mm. pressure if the electric force were great enough. But in so moving it collides x times with oxygen molecules, and x has been found equal to 7.06 (equation (6) above). It follows that the impinging electron, no matter how great its velocity, can only dissociate into atoms an oxygen molecule at, roughly,* every other impact. This result admits of an obvious explanation if the dissociation of the molecule is attributed to the mechanical effects of the collision. For the colliding electron would not separate the two atoms of the molecule unless the impulse due to the collision carried the atom struck away from its companion atom. But, however the two atoms may move together as one dynamical system, a blow concentrated at a point, such as that due to an impinging electron, and applied at random to the moving molecule, would drive the atom that received the blow towards the other atom just about as often, probably, as away from it. Hence only about half the number of collisions that an electron makes with oxygen molecules, with sufficient velocity to dissociate them, can succeed in doing so.

Effects of Temperature upon Chemical Activity.

A few experiments were made to ascertain the effect of temperature upon the chemical activity of the discharge. The discharge tube was surrounded by a vessel containing a freezing mixture, and the value of W determined at pressures of about 0.7 mm. The result showed that the total activity was lowered by lowering the temperature, but by only a percentage not exceeding the percentage diminution in the absolute temperature.

General Discussion.

The theory developed above, which attributes the chemical action in the positive column to the action of electrons alone, is sufficient to explain fully all the complicated effects therein observed in electrolytic gas. According to

* Or, perhaps, accurately ; since, as shown in connection with equation (6), the value 7.06 of x may involve a large percentage error. [Since this note was written, Prof. Townsend's 'Ionisation of Gases by Collision' has come to hand containing (p. 24,*f*) revised numbers. These would make $x = 7.6$, so that "roughly" may perhaps be omitted. It should be added that the value of $1/\lambda$ of equation (7) is scarcely affected, the new numbers giving 10.9 instead of 10.7.]

it, an electron is capable by collision of breaking up an oxygen molecule into uncharged atoms, just as Prof. Townsend has shown it can break up a molecule into ions. It follows from the numerical results that the same collision might at once both atomise and ionise a molecule; another collision might have either of these two effects without the other, according to the velocity and other circumstances of the impact. For the work* required to ionise a molecule of a gas, except in peculiarly favourable circumstances of ionic impact, is much greater than the work needed to dissociate a molecule of oxygen into atoms; and, on the other hand, ionisation may occur at every impact, if the velocity is great enough, but not dissociation into atoms.

Again, since positive† ions have also the power of ionising molecules by collision, it is highly probable that they can perform the task, lighter in respect of work to be done, of breaking up molecules of oxygen into atoms, if they are moving in a strong enough field of force. Thus it is possible that the great chemical activity in a discharge across the cathode fall may be the work of the positive ions, though there is no direct evidence of this.

With regard to other reactions produced by an electric discharge, it is natural to assume that the part played by it in promoting chemical action is the same.

The collisions of the ions, probably both kinds, with the molecules of gas bring the gas into the active state, either by dissociating or displacing the atoms, so that it can form new combinations. It follows that different chemical products might be formed in the same gaseous mixture by the motion of ions under different fields of force.

This theory does not dispense with the postulate of chemical forces acting selectively, but only explains how the discharge prepares the way for their action. On the contrary, it was pointed out above that the experimental results, quite independently of theory, lead certainly to the conclusion that the atoms of oxygen when separated are not charged electrically, so that it is necessary to postulate some other force that binds them into a molecule.

The connection between w , p , and Y , expressed in equation (4), owes its form partly to the fact involved in the theory that only one of the constituents of electrolytic gas (viz., oxygen) has to be brought to the active state in order to produce the reaction. In fact the quantity m_1 of one of the components of a gaseous mixture M that can be brought to any active

* J. S. Townsend, 'Phil. Mag.' [5], 1903.

† J. S. Townsend, 'Phil. Mag.', November, 1903.

state A by the motion through 1 cm. of an ion (of either kind) under an electric force X must satisfy Townsend's functional equation*

$$m_1/p = f(X/p), \quad (11)$$

since m_1 is obviously proportional to the number of collisions which the ion makes per centimetre of a certain type, namely, the type of collision which owing to the velocity and other circumstances of impact can bring the molecule struck to the state A. Equation (4) is of the functional form (11), as must evidently be the case, since the quantity of water w , formed per centimetre of the electron's motion, is proportional simply to the amount of oxygen brought to the active state per centimetre of that motion.

If, however, the reaction between two constituents of the gaseous mixture M set up in a gas by a current can only take place if both constituents are brought to an active state different from their ordinary condition, then, by the law of mass action, the amount m of the chemical product formed per centimetre of the ion's motion will be proportional to the product of m_1 and m_2 , where m_2 is the quantity of the other reacting substance brought to the active state per centimetre of the ion's motion. And since

$$m_2/p = \phi(X/p),$$

therefore

$$m/p^2 = \psi(X/p).$$

Similarly, if three substances combine under the same conditions, the mass of the product formed per centimetre of the ion's motion would satisfy $m/p^3 = \chi(X/p)$, and so on.

The total amount of a chemical product formed per second by a gaseous electric current of either sign is obtained by a volume integration when ν , the chemical activity at any point P (mass of the product resulting from the flow of unit quantity of electricity past the point per centimetre of that flow) is known in terms of the pressure p and the electric force X at P. For if ρ is the density of the ionic stream past P and u its velocity, the quantity of electricity that passes a small area δA perpendicular to the direction of the current is $epu \delta A$ per second; and this after flowing a distance δs will give rise to the mass $\nu epu \delta A \delta s$ of the product. Hence the whole product per second produced by the current will be

$$\int \nu e p u d\tau,$$

where $d\tau$ is the element of volume at the point P. In the general case where the current consists of two streams of positive and negative ions, the total chemical product per second of the current will consist of the sum of two such

* J. S. Townsend, 'Phil. Mag.', February, 1901.

volume integrations. If ν applies to the effects of the motion of a single ion, e must of course be replaced by unity.

In the case of such currents as can be made (*e.g.* by means of the Röntgen rays, ultra-violet light, radium, &c.) to pass between two electrodes without disturbing the electrostatic field, ρ is so small that the mass of the chemical product would not be detectable. It is only in the case of very much larger currents, such as those maintained through a gas by a battery, or those obtained by connecting the electrodes to the secondary terminals of a Ruhmkorff coil, as in the case of the silent discharge, that a sufficient number of effective collisions are made by the ions traversing the gas to produce a measurable effect.

Summary of Principal Conclusions.

(1) When a steady discharge passes through electrolytic gas at pressure p mm., the number of molecules of water vapour formed by the passage of the atomic charge through 1 cm. of the positive column, where the electric force is Y , is approximately $7.9pe^{-42.7p/Y}$. This number, which is independent of the current, appears to be absolute (*i.e.* independent of the apparatus and not confined to positive columns) and to depend only upon the field of force.

(2) The atoms of oxygen, when separated, are not charged electrically. This is proved by experiments independently of theory. Hence the atom of oxygen is not bound in a molecule of water vapour by electrostatic force.

(3) The chemical effects, within the positive column, are due to the collisions of the (corpuseular) negative ions with the oxygen molecules, which are dissociated into atoms, under certain conditions, by those collisions, and so enabled to combine with hydrogen.

(4) The energy of formation of an oxygen molecule is less than 6.1×10^{-12} ergs, and is nearly equal to 5.3×10^{-12} ergs.

(5) Water vapour is produced by the collision of an atom of oxygen with a *molecule* of hydrogen.

(6) The energy of formation of a molecule of water vapour is nearly 6.4×10^{-12} ergs.

(7) Only half the collisions that an electron makes with a molecule of oxygen, with sufficient velocity to dissociate it, succeed in doing so.

In conclusion, the writer wishes to express his many obligations to the work of Prof. Townsend, whose researches on the ionisation of gases by collision have made possible the present research (which was carried out in his laboratory) and to thank him for his suggestions. He also wishes to express his obligations to Mr. A. F. Walden, Fellow of New College, for some valuable information.
